Supporting Information

Prediction of the Structures and Heats of Formation of MO_2, MO_3, and M_2O_5 for M = V, Nb, Ta, Pa

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Geometry analysis of $MO_2(OH)$ and MF_5 species

The optimized geometries for $MO_2(OH)$ and MF_5 M = V, Nb, Ta, and Pa at the DFT/B3LYP level are shown in Figure S1 and S2, respectively. The addition of a H forms a non-planar $MO_2(OH)$ for M = V, Nb, and Ta, with two axial V=O bonds differing by only 0.002 Å and a M-OH bond distance 0.2 Å longer. The DFT optimized geometry of $PaO_2(OH)$ has been previously reported (see text reference 94). In contrast to the other group 5 metals, $PaO_2(OH)$ is a planar molecule with almost identical Pa-O axial bond lengths and an equatorial Pa-OH bond longer by about 0.3 Å. The ∠O-M-O is largest in Pa molecule followed by V, and smaller nearly identical angles shared by Nb and Ta. The predicted geometries for the MF_5 molecules are all D_{3h}, with increasing M-F bond lengths as we go down the group. The equatorial M-F bonds are equal in length and are on average 0.03 Å shorter than the axial M-F bonds in the V, Nb, and Ta pentafluorides. In PaF_5 the axial M-F bonds are just slightly shorter compared to the equatorial bonds.

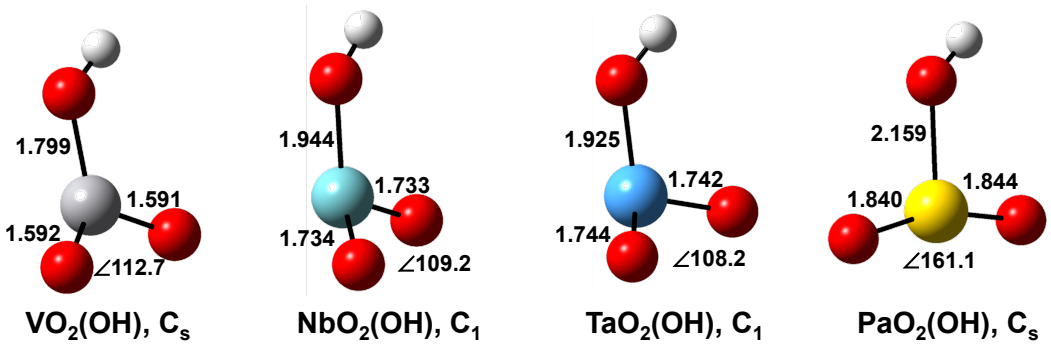

Figure S1. Optimized geometries for $MO_2(OH)$, M = V, Nb, Ta, and Pa. H atoms in white, O atoms in red, V atom in silver, Nb atom in teal, Ta atom in blue, and Pa atom in gold.

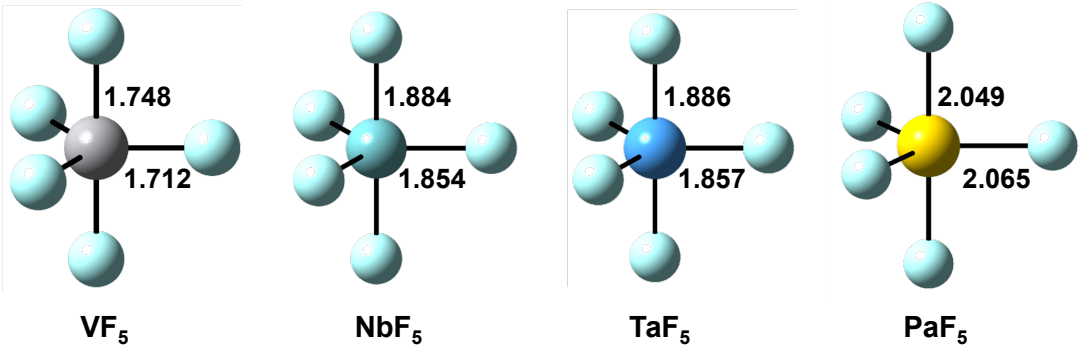

Figure S2. Optimized geometries for MF_5, M = V, Nb, Ta, and Pa. F atoms in cyan, V atom in silver, Nb atom in teal, Ta atom in blue, and Pa atom in gold.

Table S1. Total Atomization Energies and Heats of Formation at 0 K and 298K at the CBS Level in kcal/mol for MO_2, MO_2^+, MO_3, MO_3^-, and $MO_2(OH)$ for M = V, Nb, Ta, and Pa, with HF and PW91 Orbitals.

	HF			PW91		
Species	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$
VO_2	279.0	-38.6	-39.1	286.8	-46.5	-46.9
VO_2^+	82.3	158.0	157.4	85.3	155.1	154.5
VO_3	369.4	-70.0	-70.8	383.0	-83.6	-83.3
VO_3^-	471.4	-172.0	-172.9	473.8	-174.4	-174.2
$VO_2(OH)$	487.5	-136.5	-137.9	490.1	-139.1	-138.5
NbO_2	333.6	-41.2	-41.8	337.2	-44.8	-45.5
NbO_2^+	150.9	141.5	140.8	150.7	141.8	141.1
NbO_3	426.7	-75.3	-76.1	431.2	-79.8	-80.6
NbO_3^-	523.9	-172.5	-173.4	524.0	-172.6	-173.4
$NbO_2(OH)$	546.4	-143.3	-144.9	546.6	-143.6	-145.1
TaO_2	339.8	-35.1 (-35.9)[a]	-35.8 (-36.7)[a]	342.4	-37.6 (-38.5)[a]	-38.4 (-39.2)[a]
TaO_2^+	141.1	163.6	162.8	140.6	164.1	163.3
TaO_3	427.9	-64.1	-65.0	431.7	-68.0	-68.8
TaO_3^-	534.6	-170.8	-171.9	534.4	-170.6	-171.7
$TaO_2(OH)$	555.2	-139.9	-141.6	555.0	-139.6	-141.3
PaO_2[b]	396.9	-142.7	-143.3	400.0	-145.8	-144.8
PaO_2^+	390.3	-0.2	-0.8	390.2	-0.1	-0.7
PaO_3[c]	481.3	-168.1	-168.8	486.9	-173.7	-174.4
PaO_3^- [d]	571.4	-258.2	-259.1	573.5	-260.3	-261.2
$PaO_2(OH)$[e]	609.3	-244.4	-245.9	609.9	-245.1	-246.6

[a] Values in parentheses at the CBS Q5 limit. [b-e] Atomization energy calculated as [b]$PaO_2 \rightarrow Pa^+ + 2O$, [c]$PaO_3 \rightarrow Pa^+ + 3O$, [d]$PaO_3^- \rightarrow Pa^+ + 3O$, [e]$PaO_2(OH) \rightarrow Pa^+ + 3O + H$, and corrected by IE(Pa).

Table S2. Ionization Energy (IE) of MO_2 at the FPD Level in eV, with HF and PW91 Orbitals.

MO_2	HF	PW91
VO_2	8.53	8.74
NbO_2	7.92	8.09
TaO_2	8.62	8.75
PaO_2	6.18	6.32

Table S3. Adiabatic Electron Affinity (AEA) of MO_3 and Vertical Detachment Energy (VDE) of MO_3^- at the FPD Level in eV, with HF and PW91 Orbitals.

MO_3	HF AEA	PW91 AEA	HF VDE	PW91 VDE
VO_3	4.42	3.94	4.63	4.21
NbO_3	4.22	4.02	4.71	4.54
TaO_3	4.63	4.45	4.72	4.59
PaO_3	3.91	3.76		

Table S4. Calculated Heats of Formation at 298K at the FPD Level for MF_5 in kcal/mol, with HF and PW91 Orbitals.

	HF			PW91		
Species	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$
VF_5 [a]	552.8	-338.0	-339.5	557.4	-342.6	-344.1
VF_5 [b]	552.8	-338.0	-339.5	557.5	-342.8	-344.3
NbF_5	674.3	-407.4	-408.8	675.1	-408.3	-409.7
TaF_5	709.8	-430.7	-432.1	710.1	-431.0	-432.3
PaF_5 [c]	748.3	-519.8	-520.7	750.0	-521.5	-522.4

[a] DKH3 Hamiltonian and associated basis sets. [b] ECP basis sets used. [c] FPD heat of formation calculated as $PaF_5 \rightarrow Pa^+ + 5F + e^-$ and corrected by IE(Pa).

Table S5. M_2O_5 Total Atomization Energies and Heats of Formation at the FPD Level at 0 K and 298K in kcal/mol, with HF and PW91 Orbitals.

		HF			PW91		
Dimer	**Isomer**[a]	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$	ΣD^0_{0K}	$\Delta H_{f,0K}$	$\Delta H_{f,298K}$
V_2O_5	di-bridge	785.0	-245.3	-246.6	790.8	-251.1	-248.2
	tri-bridge	778.1	-238.4	-239.7	783.9	-244.2	-241.3
	mono-bridge	762.6	-222.9	-224.2	768.4	-228.7	-225.8
Nb_2O_5	di-bridge	906.4	-262.5	-263.9	906.0	-262.5	-264.9
	tri-bridge	903.7	-259.8	-261.2	903.7	-259.8	-261.2
	mono-bridge	882.5	-238.6	-240.0	882.5	-238.6	-240.0
Ta_2O_5	tri-bridge	935.8	-267.3	-268.8	935.4	-266.9	-268.5
	di-bridge	929.1	-260.6	-262.1	928.7	-260.2	-261.8
	mono-bridge	899.5	-231.0	-232.5	899.1	-230.6	-232.2
Pa_2O_5	tri-bridge	1042.0	-474.6	-475.7	1043.5	-476.1	-477.2
	di-bridge	1029.3	-461.9	-463.0	1030.8	-463.4	-464.5
	mono-bridge[b]	1007.8	-440.1	-441.5	1009.2	-441.8	-442.9

[a] Atomization energy obtained by relative energies from the mono-bridge isomer. [b] FPD atomization energy calculated for this isomer as $Pa_2O_5 \rightarrow 2Pa^+ + 5O$ and corrected by the IE(Pa).

Table S6. $\Delta H_{rxn,298K}$ in kcal/mol for the Reaction (7) and (8) at the FPD Level with HF and PW91 Orbitals.[a]

	$\Delta H_{rxn,298K}$ Reaction (7)		$\Delta H_{rxn,298K}$ Reaction (8)			
M	**HF**	**PW91**	**HF**	**eV**	**PW91**	**eV**
V	-28.7	-29.0	231.2	10.03	228.5	9.91
Nb	-31.9	-31.8	231.3	10.03	231.6	10.04
Ta	-43.5	-44.6	253.1	10.97	253.8	11.01
Pa	-41.6	-41.8	203.1	8.81	202.6	8.79

[a] $\Delta H_{f,298K}(H_2O)$ = -57.8 kcal/mol. See text for references

Table S7. Average M=O BDEs and M–O BDEs in kcal/mol at the FPD Level with the HF and PW91 Orbitals.

	HF	PW91	HF	PW91
M	**BDE(M=O)**	**BDE(M=O)**	**BDE(M-O)**	**BDE(M-O)**
V	140	143	102	97
Nb	167	169	108	104
Ta	170	171	110	107
Pa	199	200	107	105

Table S8. Atomic Thermal Correction in kcal/mol.

Atoms	**Atomic Thermal Correction**	**Ref.**
H	1.01	89
O	1.04	89
F	1.05	89
V	1.10	88
Nb	1.25	88
Ta	1.36	88
Pa	1.54	88

Table S9. Electronic Energies in Hartrees for V Molecules at the CCSD(T) Level with HF Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**w5-DK**	**CBS DTQ**	**CBS Q5**
VO_2	-1098.980350	-1099.235058	-1099.304620	-1099.329145	-1099.342817	-1099.349059
VO_2^+	-1098.671219	-1098.925033	-1098.993560	-1099.017705	-1099.031087	-1099.037310
VO_3	-1174.134690	-1174.467990	-1174.559404	-1174.590675	-1174.609648	-1174.616068
VO_3^-	-1174.290207	-1174.627749	-1174.721413	-1174.753396	-1174.773031	-1174.779367
VO_2(OH)	-1174.822680	-1175.163030	-1175.256835	-1175.289511	-1175.308451	-1175.316044
V_2O_5, mono-bridge	-2273.295755	-2273.887017	-2274.049640		-2274.139080	

Table S10. Electronic Energies in Hartrees for V Molecules at the CCSD(T) Level with PW91 Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**w5-DK**	**CBS DTQ**	**CBS Q5**
VO_2	-1098.988851	-1099.241769	-1099.310336	-1099.334387	-1099.347921	-1099.353916
VO_2^+	-1098.671104	-1098.923589	-1098.991332	-1099.015115	-1099.028375	-1099.034426
VO_3	-1174.151360	-1174.483703	-1174.574300	-1174.605187	-1174.624024	-1174.630268
VO_3^-	-1174.289080	-1174.625404	-1174.718350	-1174.749968	-1174.769525	-1174.775643
VO_2(OH)	-1174.821945	-1175.161007	-1175.254070	-1175.285496	-1175.305229	-1175.311014
V_2O_5, mono-bridge	-2273.295258	-2273.884068	-2274.045208		-2274.133731	

Table S11. Electronic Energies in Hartrees for Nb Molecules at the CCSD(T) Level with HF Orbitals.

	wD-PP	**wT-PP**	**wQ-PP**	**w5-PP**	**CBS DTQ**	**CBS Q5**
NbO_2	-206.915031	-207.160498	-207.231008	-207.255827	-207.270167	-207.275980
NbO_2^+	-206.629708	-206.874364	-206.944515	-206.969353	-206.983459	-206.989522
NbO_3	-282.022574	-282.348267	-282.441052	-282.472849	-282.492489	-282.498668
NbO_3^-	-282.170855	-282.500596	-282.595525	-282.627978	-282.648272	-282.654330
NbO_2(OH)	-282.714292	-283.046910	-283.142115	-283.174450	-283.194948	-283.200706
Nb_2O_5, mono-bridge	-489.131425	-489.708306	-489.873722	-489.930694	-489.965554	-489.976955

Table S12. Electronic Energies in Hartrees for Nb Molecules at the CCSD(T) Level with PW91 Orbitals.

	wD-PP	**wT-PP**	**wQ-PP**	**w5-PP**	**CBS DTQ**	**CBS Q5**
NbO_2	-206.920801	-207.166107	-207.236556	-207.261348	-207.275680	-207.281479
NbO_2^+	-206.629866	-206.874213	-206.944329	-206.969149	-206.983261	-206.989303
NbO_3	-282.029557	-282.355361	-282.448110	-282.479884	-282.499520	-282.505684
NbO_3^-	-282.171422	-282.500826	-282.595750	-282.628187	-282.648506	-282.654525
NbO_2(OH)	-282.714801	-283.047087	-283.142280	-283.174590	-283.195116	-283.200826
Nb_2O_5, mono-bridge	-489.132727	-489.708979	-489.874326	-489.931258	-489.966133	-489.977487

Table S13. Electronic Energies in Hartrees for Ta Molecules at the CCSD(T) Level with HF Orbitals.

	wD-PP	**wT-PP**	**wQ-PP**	**w5-PP**	**CBS DTQ**	**CBS Q5**
TaO_2	-207.523041	-207.767183	-207.837486	-207.862630	-207.876551	-207.883048
TaO_2^+	-207.210939	-207.453878	-207.523942	-207.549081	-207.562888	-207.569494
TaO_3	-282.616634	-282.941810	-283.034730	-283.066942	-283.086276	-283.093098
TaO_3^-	-282.780575	-283.109341	-283.204170	-283.237000	-283.256883	-283.263659
TaO_2(OH)	-283.322055	-283.653545	-283.748737	-283.781483	-283.801601	-283.808073
Ta_2O_5, mono-bridge	-490.345852	-490.920745	-491.085965	-491.143889	-491.177733	-491.190924

Table S14. Electronic Energies in Hartrees for Ta Molecules at the CCSD(T) Level with PW91 Orbitals.

	wD-PP	**wT-PP**	**wQ-PP**	**w5-PP**	**CBS DTQ**	**CBS Q5**
TaO_2	-207.527511	-207.771553	-207.841819	-207.866944	-207.880863	-207.881558
TaO_2^+	-207.210614	-207.453242	-207.523291	-207.548417	-283.092589	-283.091977
TaO_3	-282.622721	-282.948138	-283.041054	-283.073257	-207.562237	-207.562979
TaO_3^-	-282.780699	-283.109154	-283.204007	-283.236831	-283.256746	-283.256181
TaO_2(OH)	-283.322131	-283.653305	-283.748513	-283.781247	-283.801399	-283.800273
Ta_2O_5, mono-bridge	-490.346184	-490.920488	-491.085733	-491.143638	-491.177538	-491.177306

Table S15. Electronic Energies in Hartrees for Pa Molecules at the CCSD(T) Level with HF Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**CBS DTQ**
PaO_2	-27375.749035	-27376.240208	-27376.394453	-27376.481714
PaO_2^+	-27375.523632	-27376.015189	-27376.169877	-27376.257424
PaO_3	-27450.886254	-27451.460723	-27451.638371	-27451.738566
PaO_3^-	-27451.030160	-27451.604596	-27451.782821	-27451.883406
PaO_2(OH)	-27451.596651	-27452.174070	-27452.353525	-27452.454840
Pa_2O_5, mono-bridge	-54826.843263	-54827.909492	-54828.243043	-54828.431599

Table S16. Electronic Energies in Hartrees for Pa Molecules at the CCSD(T) Level with PW91 Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**CBS DTQ**
PaO_2	-27375.742956	-27376.225661	-27376.374784	-27376.458873
PaO_2^+	-27375.512828	-27375.995551	-27376.145127	-27376.229523
PaO_3	-27450.883853	-27451.450184	-27451.622728	-27451.719752
PaO_3^-	-27451.023265	-27451.588616	-27451.761653	-27451.859044
PaO_2(OH)	-27451.587137	-27452.155611	-27452.329946	-27452.428107
Pa_2O_5, mono-bridge	-54826.824679	-54827.873037	-54828.196319	-54828.378549

Table S17. Electronic Energies in Hartrees for Dimer Isomers at the CCSD(T) Level with HF Orbitals.

M_2O_5	**Isomer**	**aD-PP**	**aT-PP**	**aQ-PP**	**CBS DTQ**
Nb_2O_5	mono-bridge	-488.352012	-488.706134	-488.816416	-488.878703
	di-bridge	-488.392273	-488.744454	-488.854569	-488.916810
	tri-bridge	-488.388038	-488.738753	-488.849668	-488.912502
Ta_2O_5	mono-bridge	-489.652479	-490.012620	-490.122237	-490.183863
	di-bridge	-489.701437	-490.059624	-490.169218	-490.230897
	tri-bridge	-489.713248	-490.069829	-490.179713	-490.241644
		aD-DK	**aT-DK**	**aQ-DK**	**CBS DTQ**
V_2O_5	mono-bridge	-2273.266695	-2273.855496	-2274.013525	-2274.099942
	di-bridge	-2273.306542	-2273.891849	-2274.049443	-2274.135687
	tri-bridge	-2273.298515	-2273.882187	-2274.038995	-2274.124765
Pa_2O_5	mono-bridge	-54825.475185	-54825.985155	-54826.126434	-54826.204263
	di-bridge	-54825.511666	-54826.018877	-54826.160413	-54826.238513
	tri-bridge	-54825.533325	-54826.038548	-54826.180428	-54826.258830

Table S18. Electronic Energies in Hartrees for MF_5 Molecules at the CCSD(T) Level with HF Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**CBS DTQ**
VF_5	-1447.771686	-1448.386793	-1448.559726	-1448.655313
PaF_5	-27724.677856	-27725.514384	-27725.771672	-27725.916625
	wD-PP	**wT-PP**	**wQ-PP**	**CBS DTQ**
VF_5	-569.893443	-570.491324	-570.663089	-570.758485
NbF_5	-555.489008	-556.089504	-556.263469	-556.360262
TaF_5	-556.142597	-556.743317	-556.917254	-557.014022
PaF_5	-938.063163	-938.941274	-939.220970	-1255.962891

Table S19. Electronic Energies in Hartrees for MF_5 Molecules at the CCSD(T) Level with PW91 Orbitals.

	wD-DK	**wT-DK**	**wQ-DK**	**CBS DTQ**
VF_5	-1447.775012	-1448.388205	-1448.560407	-1448.655566
PaF_5	-27724.670980	-27725.497839	-27725.750008	-27725.891835
	wD-PP	**wT-PP**	**wQ-PP**	**CBS DTQ**
VF_5	-569.903138	-570.499937	-570.671706	-570.767143
NbF_5	-555.491270	-556.091031	-556.265030	-556.361872
TaF_5	-556.143935	-556.743998	-556.917998	-557.014831
PaF_5	-938.067249	-938.944896	-939.224640	-939.383358

Table S20. Total Atomization Energies for Heats of Formation of Ta Species with HF And PW91 Orbitals in kcal/mol.

	wD-PP	wT-PP	wQ-PP	w5-PP	CBS (DTQ)	CBS (Q5)
TaO_2						
HF	334.1	348.5	353.8	355.9	356.9	357.7
PW91	336.8	351.1	356.4	358.5	359.4	360.3
TaO_2^+						
HF	138.2	151.9	157.0	159.2	160.0	160.9
PW91	138.0	151.4	156.5	158.6	159.5	160.4
TaO_3						
HF	416.7	435.4	442.5	445.2	446.6	447.4
PW91	420.5	439.3	446.3	449.0	450.4	451.2
TaO_3^-						
HF	519.6	540.5	548.8	551.9	553.7	554.4
PW91	519.6	540.3	548.6	551.8	553.4	554.2
$TaO_2(OH)$						
HF	545.6	568.3	576.8	579.8	581.7	582.3
PW91	545.6	568.0	576.5	579.6	581.5	582.0
Ta_2O_5						
HF	880.2	916.7	930.4	935.6	938.3	939.9
PW91	880.3	916.4	930.0	935.2	937.9	939.5

aug-cc-pwCVNZ (O)/cc-pwCVNZ-PP (Ta), abbreviated as wN-PP (N = D, T, Q, 5)

Table S21. Components to Calculated Atomized Ta Species ΔE_{ecp} Corrections Calculate with HF Orbitals. ΔE_{ZPE}, Atomic ΔE_{SO} and molecular Thermal (TC) Correction Values.

Species	wT-PP	wT-DK4f [a]	ΔE_{ecp}	ΔE_{ZPE}	$\Delta E_{SO\ atoms}$	TC_{mol}
TaO_2	348.5	345.3	-3.2	-3.2	-10.6	2.7
TaO_2^+	151.9	147.0	-4.8	-3.4	-10.6	3.6
TaO_3	435.4	431.6	-3.8	-4.1	-10.9	2.6
TaO_3^-	540.5	537.0	-3.6	-4.7	-10.9	3.4
$TaO_2(OH)$	568.3	564.2	-4.1	-11.6	-10.9	3.8
Ta_2O_5	916.7	908.7	-8.0	-9.3	-21.5	6.3

[a] aug-cc-pwCVTZ (O)/cc-pwCVTZ-DK (Ta) with added Ta tight functions and 4f correlated, abbreviated as wT-DK4f.

Table S22. TAEs and Heats of Formation Calculated of Ta species at the CCCSD(T)/CBS Q5, with HF and PW91 Orbitals.

	HF			PW91		
Species	**$\Sigma D_{0,0K}$**	**ΔH_{0K}**	**ΔH_{298K}**	**$\Sigma D_{0,0K}$**	**ΔH_{0K}**	**ΔH_{298K}**
TaO_2	340.6	-35.9	-36.7	343.2	-38.5	-39.2
TaO_2^+	142.1	162.7	161.9	141.5	163.3	162.4
TaO_3	428.7	-65.0	-65.8	432.5	-68.8	-69.7
TaO_3^-	535.4	-171.6	-172.7	535.1	-171.4	-172.4
$TaO_2(OH)$	555.8	-140.5	-142.2	555.6	-140.2	-141.9
Ta_2O_5, mono-bridge	901.0	-232.5	-234.1	900.6	-232.1	-233.7

Table S23. ΔH_{0K} Comparisons in kcal/mol for TaO_2 at Various CBS Limit Calculated with HF and PW91 Orbitals.

Method	**CBS**	**HF**	**PW91**
$Ta + 2O \rightarrow TaO_2$	DTQ	-38.2	-40.8
$Ta + 2O \rightarrow TaO_2$	DTQ+ECP	-35.1	-37.6
$Ta + O_2 \rightarrow TaO_2$	DTQ	-38.4	-41.0
$Ta + O_2 \rightarrow TaO_2$	DTQ + ECP	-35.4	-38.0
$Ta + 2O \rightarrow TaO_2$	TQ	-38.2	-40.8
$Ta + 2O \rightarrow TaO_2$	TQ + ECP	-35.0	-37.6
$Ta + O_2 \rightarrow TaO_2$	TQ	-38.7	-41.3
$Ta + O_2 \rightarrow TaO_2$	TQ + ECP	-35.7	-38.3
$Ta + 2O \rightarrow TaO_2$	Q5	-39.0	-41.6
$Ta + 2O \rightarrow TaO_2$	Q5 + ECP	-35.9	-38.5
$Ta + O_2 \rightarrow TaO_2$	Q5	-39.7	-42.3
$Ta + O_2 \rightarrow TaO_2$	Q5 + ECP	-36.7	-39.3
$Ta + O_2 \rightarrow TaO_2$ [a]	TQ	-39.3	
$Ta + O_2 \rightarrow TaO_2$ [a]	Q5	-40.3	
$Ta + O_2 \rightarrow TaO_2$ [b]	Q5 + ECP	-37.3	

[a] Ref. 86. [b] Value from Ref. 86 corrected by current ΔE_{ECP}.

Table S24. ΔH_{0K} Comparisons in kcal/mol for $TaO_2(OH)$ at Various CBS Limits Calculated with HF and PW91 Orbitals.

Method	CBS	HF	PW91
$Ta + 3O + H \rightarrow TaO_2(OH)$	DTQ	-143.9	-143.7
$Ta + 3O + H \rightarrow TaO_2(OH)$	DTQ + ECP	-139.9	-139.6
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	DTQ	-143.7	-143.4
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	DTQ + ECP	-140.1	-139.8
$Ta + 3O + H \rightarrow TaO_2(OH)$	TQ	-143.9	-143.6
$Ta + 3O + H \rightarrow TaO_2(OH)$	TQ + ECP	-139.8	-139.5
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	TQ	-144.0	-143.7
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	TQ + ECP	-140.4	-140.1
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$	TQ	-142.8	-142.5
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$	TQ + ECP	-139.5	-139.3
$Ta + 3O + H \rightarrow TaO_2(OH)$	Q5	-144.5	-144.2
$Ta + 3O + H \rightarrow TaO_2(OH)$	Q5 + ECP	-140.5	-140.2
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	Q5	-145.1	-144.7
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	Q5 + ECP	-141.5	-141.1
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$	Q5	-144.6	-144.2
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$	Q5 +ECP	-141.4	-140.9
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$ [a]	TQ	-144.9	
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$ [a]	Q5	-146.0	
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$ [b]	Q5 + ECP	-142.4	
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$ [a]	TQ	-143.2	
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$ [a]	Q5	-145.1	
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$ [b]	Q5 + ECP	-141.8	

[a] Ref. 94. [b] Value from Ref. 94 corrected by current ΔE_{ECP}.

Table S25. ΔE_{ECP} Corrections for TaO_2 and $TaO_2(OH)$ Reactions.

Reaction	ΔE_{ECP} kcal/mol
$Ta + 2O \rightarrow TaO_2$	3.2
$Ta + O_2 \rightarrow TaO_2$	3.0
$Ta + 3O + H \rightarrow TaO_2(OH)$	4.1
$Ta + O_2 + H_2O \rightarrow TaO_2(OH) + H$	3.6
$Ta + 3H_2O \rightarrow TaO_2(OH) + 5H$	3.3

Table S26. Total Atomization Energies in kcal/mol for Heats of Formation of Nb Species with HF and PW91 Orbitals.[a]

Species	wD-PP	wT-PP	wQ-PP	w5-PP	CBS (DTQ)	CBS (Q5)
NbO_2						
HF	316.3	329.1	333.4	335.3	335.9	336.7
PW91	319.9	332.6	336.9	338.7	339.3	340.2
NbO_2^+						
HF	137.2	149.6	153.7	155.5	156.0	157.0
PW91	137.3	149.5	153.5	155.3	155.9	156.8
NbO_3						
HF	407.6	424.3	430.2	432.5	433.6	434.4
PW91	412.0	428.8	434.6	436.9	437.9	438.8
NbO_3^-						
HF	500.7	519.9	527.1	529.9	531.3	532.1
PW91	501.0	520.0	527.2	530.0	531.4	532.2
$NbO_2(OH)$						
HF	528.0	549.0	556.4	559.0	560.6	561.2
PW91	528.3	549.1	556.4	559.1	560.7	561.2
Nb_2O_5						
HF	845.5	878.7	890.2	894.6	896.8	898.1
PW91	846.4	879.1	890.5	894.8	897.1	898.4

[a] aug-cc-pwCVNZ (O)/cc-pwCVNZ-PP (Nb), abbreviated as wN-PP (N = D, T, Q, 5).

Table S27. Components to Calculated Atomized Nb Species ΔE_{ECP} Corrections, with HF Orbitals, ΔE_{ZPE}, and Atomic ΔE_{SO} Values, in kcal/mol.[a]

Species	wT-PP	wT-DK	ΔE_{ecp}	ΔE_{ZPE}	ΔE_{SO}	TC $_{mol}$
NbO_2	329.1	329.4	0.3	-3.3	0.7	2.7
NbO_2^+	149.6	150.3	0.7	-3.5	-2.3	2.6
NbO_3	424.3	424.4	0.1	-4.4	-2.5	3.5
NbO_3^-	519.9	519.7	-0.3	-4.6	-2.5	3.5
$NbO_2(OH)$	549.0	548.8	-0.2	-11.6	-2.5	3.8
Nb_2O_5, mono-bridge	878.7	878.5	-0.2	-9.4	-4.7	6.3

[a] aug-cc-pwCVTZ-DK (O)/ cc-pwCVNZ-DK (Nb), abbreviated as wT-DK.

Table S28. TAEs and Heats of Formation Calculated for Nb species in kcal/mol at the CCCSD(T)/CBS Q5 with HF and PW91 Orbitals.

	HF			PW91		
Species	**$\Sigma D_{0,0K}$**	**ΔH_{0K}**	**ΔH_{298K}**	**$\Sigma D_{0,0K}$**	**ΔH_{0K}**	**ΔH_{298K}**
NbO_2	334.5	-42.0	-42.7	338.1	-45.6	-46.3
NbO_2^+	151.9	140.5	139.8	151.6	140.8	140.1
NbO_3	427.6	-76.1	-77.0	432.1	-80.6	-81.4
NbO_3^-	524.7	-173.3	-174.2	524.7	-173.3	-174.2
NbO_2(OH)	547.0	-143.9	-145.5	546.9	-143.9	-145.4
Nb_2O_5, mono-bridge	883.8	-239.9	-241.3	883.8	-239.9	-241.3

Table S29. Total Atomization Energies in kcal/mol for Heats of Formation of V Species with HF and PW91 Orbitals.[a]

Species	**wD-DK**	**wT-DK**	**wQ-DK**	**w5-DK**	**CBS (DTQ)**	**CBS (Q5)**
VO_2						
HF	263.0	274.8	280.0	282.0	283.2	283.6
PW91	271.4	282.9	288.0	289.9	291.0	291.0
VO_2^+						
HF	69.0	80.2	84.8	86.6	87.6	88.0
PW91	72.0	83.3	87.8	89.5	90.5	90.6
VO_3						
HF	351.0	365.4	371.8	374.1	375.6	376.0
PW91	364.5	379.2	385.5	387.8	389.3	389.0
VO_3^-						
HF	448.6	465.7	473.5	476.2	478.2	478.5
PW91	450.9	468.1	475.9	478.6	480.6	480.2
VO_2(OH)						
HF	469.0	487.8	495.7	498.9	500.4	501.5
PW91	471.5	490.4	498.3	500.9	503.0	502.5
V_2O_5, mono-bridge						
HF	727.4	755.6	768.3		775.9	
PW91	733.1	761.6	774.2		781.8	

[a] aug-cc-pwCVNZ-DK (O)/cc-pwCVNZ-DK (V), abbreviated as wN-DK (N = D, T, Q, 5)

Table S30. ΔE_{ZPE}, ΔE_{SO}, and Thermal (TC) Corrections in kcal/mol for V species.

Species	ΔE_{ZPE}	ΔE_{SO}	TC
VO_2	-3.3	-0.89	2.7
VO_2^+	-3.9	-1.35	2.6
VO_3	-4.7	-1.57	3.5
VO_3^-	-5.2	-1.57	3.4
$VO_2(OH)$	-11.6	-1.35	3.8
VF_5	-7.8	-2.9	4.9
V_2O_5, mono-bridge	-10.4	-2.92	6.1

Table S31. TAEs and Heats of Formation in kcal/mol for V Species at the CCCSD(T)/ CBS Q5 with HF and PW91 Orbitals.

	HF			PW91		
Species	$\Sigma D_{0,0K}$	ΔH_{0K}	ΔH_{298K}	$\Sigma D_{0,0K}$	ΔH_{0K}	ΔH_{298K}
VO_2	279.5	-39.1	-39.6	287.3	-46.9	-47.4
VO_2^+	82.8	157.6	157.0	85.7	154.6	154.0
VO_3	369.7	-70.4	-71.1	383.4	-84.0	-83.7
VO_3^-	471.7	-172.3	-173.7	474.1	-174.7	-174.5
$VO_2(OH)$	488.6	-137.6	-139.0	490.2	-139.2	-138.6

Table S32. Total Atomization Energies in kcal/mol for Heats of Formation of Pa Species with HF and PW91 Orbitals.[a]

Species	wD-DK	wT-DK	wQ-DK	CBS (DTQ)
PaO_2				
HF	536.1	541.4	545.7	548.4
PW91	539.6	545.2	549.1	551.5
PaO_2^+				
HF	394.7	400.2	404.8	407.7
PW91	395.2	400.8	405.0	407.6
PaO_3				
HF	613.4	624.2	630.7	634.6
PW91	619.2	630.6	636.5	640.2
PaO_3^-				
HF	703.7	714.5	721.3	725.5
PW91	706.7	717.4	723.7	727.6
$PaO_2(OH)$				
HF	745.9	758.2	765.7	770.3
PW91	746.7	759.5	766.6	770.9
Pa_2O_5, mono-bridge				
HF	1280.1	1296.5	1308.3	1315.7
PW91	1283.0	1299.5	1310.4	1317.1

[a] aug-cc-pwCVNZ-DK(O)/cc-pwCVNZ-DK(Pa), abbreviated as wN-DK (N = D, T, Q)

Table S33. ΔE_{ZPE}, ΔE_{SO} and Thermal (TC) Corrections in kcal/mol for Pa Species.

Species	ΔE_{ZPE}	ΔE_{SO}	TC_{mol}
PaO_2	-2.8	-12.8	3.1
PaO_2^+	-3.1	-14.3	3.0
PaO_3	-3.4	-14.6	3.9
PaO_3^-	-3.7	-14.6	3.8
$PaO_2(OH)$	-10.7	-14.6	4.2
Pa_2O_5, mono-bridge	-7.3	-28.9	7.2

Table S34. Natural Charges and Electron Configurations of MO_2^+ and MO_3^-, M = V, Nb, Ta, and Pa Calculated from NPA.

Molecule	Natural Charge	Natural Electron Configuration
VO_2^+		
V	1.99	4s(0.05)3d(2.94)
O	-0.50	2s(1.92)2p(4.55)
O	-0.50	2s(1.92)2p(4.55)
VO_3^-		
V	1.98	4s(0.10)3d(2.89)
O	-0.99	2s(1.89)2p(5.08)
O	-0.99	2s(1.89)2p(5.08)
O	-0.99	2s(1.89)2p(5.08)
NbO_2^+		
Nb	2.39	5s(0.04)4d(2.55)
O	-0.69	2s(1.91)2p(4.75)
O	-0.69	2s(1.91)2p(4.75)
NbO_3^-		
Nb	2.50	5s(0.06)4d(2.39)
O	-1.17	2s(1.91)2p(5.23)
O	-1.17	2s(1.91)2p(5.23)
O	-1.17	2s(1.91)2p(5.23)
TaO_2^+		
Ta	2.60	6s(0.07)5d(2.30)
O	-0.80	2s(1.91)2p(4.85)
O	-0.80	2s(1.91)2p(4.85)
TaO_3^-		
Ta	2.62	6s(0.11)5d(2.24)
O	-1.21	2s(1.90)2p(5.27)
O	-1.21	2s(1.90)2p(5.27)
O	-1.21	2s(1.90)2p(5.27)
PaO_2^+		
Pa	2.62	7s(0.04)5f(1.50)6d(0.88)
O	-0.81	2s(1.87)2p(4.92)
O	-0.81	2s(1.87)2p(4.92)
PaO_3^-		
Pa	2.47	7s(0.04)5f(0.95)6d(1.52)
O	-1.16	2s(1.88)2p(5.25)3d(0.02)
O	-1.16	2s(1.88)2p(5.25)3d(0.02)
O	-1.16	2s(1.88)2p(5.25)3d(0.02)

Table S35. Natural Charges and Electron Configurations of V_2O_5 Isomers Calculated from NPA.

Isomer	Natural Charge	Natural Electron Configuration
Mono-bridge, C_2		
V	2.03	4s(0.10)3d(2.86)
V	2.03	4s(0.10)3d(2.86)
O_{br}	-1.22	2s(1.83)2p(5.35)
O_{term}	-0.71	2s(1.89)2p(4.79)
O_{term}	-0.71	2s(1.89)2p(4.79)
O_{term}	-0.71	2s(1.89)2p(4.80)
O_{term}	-0.71	2s(1.89)2p(4.80)
Di-bridge, C_s		
O_{br}	-0.90	2s(1.85)2p(5.02)
O_{br}	-0.90	2s(1.85)2p(5.02)
O_{term}	-0.62	2s(1.89)2p(4.71)
O_{term}	-0.71	2s(1.87)2p(4.81)
V	1.86	4s(0.15)3d(2.98)
V	1.97	4s(0.13)3d(2.90)
O_{term}	-0.69	2s(1.87)2p(4.79)
Tri-bridge, C_1		
O_{br}	-0.90	2s(1.84)2p(5.02)
O_{br}	-0.85	2s(1.85)2p(4.97)
O_{br}	-0.90	2s(1.84)2p(5.02)
O_{term}	-0.62	2s(1.86)2p(4.73)
V	1.95	4s(0.17)3d(2.86)
O_{term}	-0.61	2s(1.86)2p(4.72)
V	1.93	4s(0.18)3d(2.88)

Table S36. Natural Charges and Electron Configurations of Nb_2O_5 Isomers Calculated from NPA.

Isomer	Natural Charge	Natural Electron Configuration
Mono-bridge, C_2		
Nb	2.55	5s(0.07)4d(2.36)
O_{br}	-1.35	2s(1.86)2p(5.47)
Nb	2.55	5s(0.07)4d(2.36)
O_{term}	-0.93	2s(1.90)2p(5.00)
O_{term}	-0.93	2s(1.90)2p(5.00)
O_{term}	-0.94	2s(1.90)2p(5.01)
O_{term}	-0.94	2s(1.90)2p(5.01)
Di-bridge, C_s		
O_{br}	-1.12	2s(1.87)2p(5.22)
O_{br}	-1.12	2s(1.87)2p(5.22)
O_{term}	-0.86	2s(1.89)2p(4.94)
O_{term}	-0.98	2s(1.89)2p(5.06)
Nb	2.52	5s(0.10)4d(2.35)
Nb	2.52	5s(0.11)4d(2.35)
O_{term}	-0.96	2s(1.89)2p(5.04)
Tri-bridge, D_{3h}		
O_{term}	-1.16	2s(1.86)2p(5.26)
O_{term}	-1.16	2s(1.86)2p(5.26)
O_{term}	-1.16	2s(1.86)2p(5.26)
O_{br}	-0.92	2s(1.87)2p(5.01)
O_{br}	-0.92	2s(1.87)2p(5.01)
Nb	2.67	5s(0.14)4d(2.16)
Nb	2.67	5s(0.14)4d(2.16)

Table S37. Natural Charges and Electron Configurations of Ta_2O_5 Isomers Calculated from NPA.

Isomer	Natural Charge	Natural Electron Configuration
Mono-bridge, C_2		
O_{br}	-1.34	2s(1.85)2p(5.47)
O_{term}	-1.00	2s(1.90)2p(5.07)
O_{term}	-1.00	2s(1.90)2p(5.07)
O_{term}	-1.01	2s(1.90)2p(5.08)
O_{term}	-1.01	2s(1.90)2p(5.08)
Ta	2.68	6s(0.12)5d(2.16)
Ta	2.68	6s(0.12)5d(2.16)
Di-bridge, C_s		
O_{br}	-1.16	2s(1.86)2p(5.25)
O_{br}	-1.16	2s(1.86)2p(5.25)
O_{term}	-0.93	2s(1.89)2p(5.00)
O_{term}	-1.07	2s(1.88)2p(5.15)
Ta	2.70	6s(0.12)5d(2.15)
Ta	2.67	6s(0.16)5d(2.12)
O_{term}	-1.06	2s(1.88)2p(5.14)
Tri-bridge, D_{3h}		
O_{br}	-1.21	2s(1.85)2p(5.31)
O_{br}	-1.21	2s(1.85)2p(5.31)
O_{br}	-1.21	2s(1.85)2p(5.31)
O_{term}	-1.02	2s(1.87)2p(5.11)
O_{term}	-1.02	2s(1.87)2p(5.11)
Ta	2.84	6s(0.17)5d(1.92)
Ta	2.84	6s(0.17)5d(1.92)

Table S38. Natural Charges and Electron Configurations of Pa_2O_5 Isomers Calculated from NPA.

Isomer	Natural Charge	Natural Electron Configuration
Mono-bridge, D_{2d}		
Pa	2.68	7s(0.05)5f(1.19)6d(1.09)
O_{br}	-1.35	2s(1.85)2p(5.48)
Pa	2.68	7s(0.05)5f(1.19)6d(1.09)
O_{term}	-1.01	2s(1.87)2p(5.10)
O_{term}	-1.01	2s(1.87)2p(5.10)
O_{term}	-1.01	2s(1.87)2p(5.10)
O_{term}	-1.01	2s(1.87)2p(5.10)
Di-bridge, C_s		
O_{br}	-1.17	2s(1.84)2p(5.31)
O_{br}	-1.17	2s(1.84)2p(5.31)
Pa	2.86	7s(0.07)5f(0.80)6d(1.27)
Pa	2.49	7s(0.08)5f(1.16)6d(1.23)
O_{term}	-0.95	2s(1.87)2p(5.04)
O_{term}	-1.03	2s(1.85)2p(5.16)
O_{term}	-1.02	2s(1.84)2p(5.14)
Tri-bridge, C_2		
Pa	2.68	7s(0.11)5f(1.09)6d(1.08)
Pa	2.68	7s(0.11)5f(1.09)6d(1.08)
O_{term}	-0.94	2s(1.84)2p(5.06)
O_{term}	-0.94	2s(1.84)2p(5.06)
O_{br}	-1.15	2s(1.83)2p(5.29)
O_{br}	-1.15	2s(1.83)2p(5.29)
O_{br}	-1.18	2s(1.83)2p(5.32)

Table S39. Natural Charges and Electron Configurations of MO_2, MO_3 and $MO_2(OH)$, M = V, Nb, Ta, and Pa Calculated from NPA.

Species	Natural Charge	Natural Electron Configuration
VO_2		
V	1.92	4s(0.07)3d(2.98)
O	-0.96	2s(1.92)2p(5.01)
O	-0.96	2s(1.92)2p(5.01)
VO_3		
V	1.92	4s(0.12)3d(2.94)
O	-0.48	2s(1.92)2p(4.54)
O	-0.72	2s(1.90)2p(4.80)
O	-0.72	2s(1.90)2p(4.80)
$VO_2(OH)$		
V	2.02	4s(0.10)3d(2.86)
O	-1.07	2s(1.79)2p(5.25)
O	-0.72	2s(1.89)2p(4.80)
O	-0.73	2s(1.89)2p(4.82)
H	0.50	1s(0.49)
NbO_2		
Nb	1.82	5s(0.56)4d(2.55)
O	-0.91	2s(1.90)2p(4.98)
O	-0.91	2s(1.90)2p(4.98)
NbO_3		
Nb	2.42	5s(0.09)4d(2.46)
O	-0.59	2s(1.94)2p(4.63)
O	-0.92	2s(1.90)2p(4.98)
O	-0.92	2s(1.90)2p(4.98)
$NbO_2(OH)$		
Nb	2.54	5s(0.07)4d(2.36)
O	-0.94	2s(1.90)2p(5.01)
O	-0.95	2s(1.90)2p(5.01)
O	-1.16	2s(1.79)2p(5.34)
H	0.51	1s(0.49)
TaO_2		
Ta	1.98	6s(0.73)5d(2.19)
O	-0.99	2s(1.90)2p(5.06)
O	-0.99	2s(1.90)2p(5.06)
TaO_3		
Ta	2.55	6s(0.16)5d(2.27)
O	-0.99	2s(1.90)2p(5.05)
O	-0.99	2s(1.90)2p(5.05)
O	-0.58	2s(1.93)2p(4.63)
$TaO_2(OH)$		

Ta	2.67	5d(2.16)7s(0.12)
O	-1.02	2s(1.90)2p(5.08)
O	-1.02	2s(1.90)2p(5.09)
O	-1.15	2s(1.79)2p(5.34)
H	0.51	1s(0.48)
PaO_2		
Pa	1.87	7s(0.88)5f(1.32)6d(0.94)
O	-0.94	2s(1.86)2p(5.05)
O	-0.94	2s(1.86)2p(5.05)
PaO_3		
Pa	2.47	7s(0.05)5f(1.34)6d(1.15)
O	-0.58	2s(1.90)2p(4.67)3d(0.01)
O	-0.94	2s(1.86)2p(5.05)3d(0.02)
O	-0.94	2s(1.86)2p(5.05)3d(0.02)
$PaO_2(OH)$		
Pa	2.60	7s(0.05)5f(1.27)6d(1.08)
O	-1.17	2s(1.79)2p(5.36)3d(0.01)
O	-0.95	2s(1.86)2p(5.06)3d(0.03)
O	-0.97	2s(1.86)2p(5.07)3d(0.03)
H	0.49	1s(0.51)

Table S40. CCSD(T) Calculated T1 Values with HF Orbitals for V and Pa Species.

	wD-DK	wT-DK	wQ-DK	w5-DK	wD-PP	wT-PP	wQ-PP
VO_2	0.055507	0.051746	0.050484	0.050151			
VO_2^+	0.042217	0.042431	0.042432	0.042503			
VO_3	0.040622	0.040032	0.039872	0.039863			
VO_3^-	0.033841	0.033972	0.033911	0.033959			
$VO_2(OH)$	0.035977	0.035968	0.035863	0.035787			
V_2O_5	0.038515	0.038626	0.038566		0.035113	0.037345	0.037306
VF_5	0.030322	0.029683	0.029438		0.029584	0.028805	0.028572
PaO_2	0.018704	0.020043	0.020526				
PaO_2^+	0.017779	0.018879	0.019318				
PaO_3	0.027494	0.027317	0.027529				
PaO_3^-	0.023920	0.025539	0.026127				
$PaO_2(OH)$	0.018955	0.019861	0.020245				
Pa_2O_5	0.019796	0.020863	0.021291		0.019087	0.020353	0.020860
PaF_5	0.018463	0.018721	0.018789		0.017903	0.018364	0.018510

Table S41. CCSD(T) Calculated T1 Values with PW91 Orbitals for V and Pa Species.

	wD-DK	wT-DK	wQ-DK	w5-DK	wD-PP	wT-PP	wQ-PP
VO_2	0.031582	0.036347	0.038335	0.038663			
VO_2^+	0.012546	0.012273	0.012361	0.012426			
VO_3	0.040542	0.042375	0.042800	0.043024			
VO_3^-	0.013202	0.013269	0.013450	0.013468			
$VO_2(OH)$	0.015828	0.015724	0.015803	0.015887			
V_2O_5	0.017359	0.017205	0.017246		0.017507	0.017245	0.017308
VF_5	0.016591	0.016995	0.017239		0.017051	0.017212	0.017449
PaO_2	0.015469	0.013915	0.013475				
PaO_2^+	0.014795	0.013136	0.012659				
PaO_3	0.030952	0.030949	0.030867				
PaO_3^-	0.021737	0.019644	0.019138				
$PaO_2(OH)$	0.018442	0.016920	0.016532				
Pa_2O_5	0.019635	0.017924	0.017469		0.019923	0.017669	0.017210
PaF_5	0.022369	0.021168	0.020946		0.022525	0.020943	0.020675

Table S42. CCSD(T) Calculated T1 Values with HF Orbitals for Nb and Ta Species.

	wD-PP	wT-PP	wQ-PP	w5-PP	wT-DK
NbO_2	0.032111	0.030919	0.030691	0.030723	0.031277
NbO_2^+	0.030903	0.030771	0.030752	0.030819	0.031268
NbO_3	0.031062	0.030264	0.030085	0.030082	0.030579
NbO_3^-	0.026467	0.026076	0.025955	0.025985	0.026437
$NbO_2(OH)$	0.026916	0.026544	0.026450	0.026488	0.026903
Nb_2O_5	0.028670	0.028400	0.028329	0.028374	0.028789
NbF_5	0.020571	0.019695	0.019417		0.019870
TaO_2	0.031006	0.030850	0.031101	0.031260	0.030353
TaO_2^+	0.028383	0.027941	0.027878	0.027918	0.027813
TaO_3	0.042797	0.040475	0.039904	0.039741	0.040253
TaO_3^-	0.025630	0.024529	0.024204	0.024151	0.024377
$TaO_2(OH)$	0.024956	0.024065	0.023837	0.023816	0.023916
Ta_2O_5	0.026448	0.025643	0.025433	0.025419	0.025474
TaF_5	0.018232	0.017118	0.016775		0.017101

Table S43. CCSD(T) Calculated T1 Values with PW91 Orbitals for Nb and Ta Species.

	wD-PP	wT-PP	wQ-PP	w5-PP	wT-DK
NbO_2	0.012775	0.012506	0.013204	0.013496	0.012904
NbO_2^+	0.010547	0.010428	0.010573	0.010619	0.010837
NbO_3	0.034030	0.034340	0.034400	0.034506	0.034168
NbO_3^-	0.014754	0.014584	0.014700	0.014679	0.015322
$NbO_2(OH)$	0.014894	0.014728	0.014827	0.015324	0.015240
Nb_2O_5	0.015887	0.015609	0.015741	0.015747	0.015609
NbF_5	0.017574	0.017681	0.017867		0.018263
TaO_2	0.014199	0.013812	0.013858	0.013868	0.013301
TaO_2^+	0.011842	0.011831	0.012017	0.012079	0.012419
TaO_3	0.034942	0.036823	0.037353	0.037568	0.036946
TaO_3^-	0.016838	0.017138	0.017367	0.017370	0.016987
$TaO_2(OH)$	0.015708	0.015901	0.016083	0.016142	
Ta_2O_5	0.016655	0.016733	0.016892	0.016922	0.010226
TaF_5	0.017165	0.017380	0.017595		0.016877

Table S44. Cartesian Coordinates in Å for B3LYP Optimized Geometries.

VO_2

V	0.000000	0.000000	0.351566
O	0.000000	1.364912	-0.505377
O	0.000000	-1.364912	-0.505377

VO_2^+

V	0.000000	0.000000	0.381905
O	0.000000	1.240433	-0.548989
O	0.000000	-1.240433	-0.548989

VO_3

V	-0.216465	-0.093186	0.000000
O	1.055267	-1.304653	0.000000
O	-0.216465	0.786281	1.340049
O	-0.216465	0.786281	-1.340049

VO_3^-

V	0.000000	0.000000	0.000000
O	0.000000	1.652233	0.000000
O	1.430875	-0.826116	0.000000
O	-1.430875	-0.826116	0.000000

VO_2(OH)

V	0.000000	0.062416	0.000000
O	1.404782	0.812016	0.000000
O	-1.265864	1.030336	0.000000
O	-0.203098	-1.725136	0.000000
H	0.513438	-2.373304	0.000000

VF_5

V	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.759741
F	0.000000	1.723456	0.000000
F	1.492557	-0.861728	0.000000
F	0.000000	0.000000	-1.759741
F	-1.492557	-0.861728	0.000000

V_2O_5 isomers

mono-bridge

V	0.000000	1.777055	0.130949
O	0.000000	0.000000	0.406762
V	0.000000	-1.777055	0.130949
O	0.542748	2.344410	-1.251105
O	-1.242359	2.611336	0.671247
O	-0.542748	-2.344410	-1.251105
O	1.242359	-2.611336	0.671247

di-bridge

V	1.464500	-0.321259	0.000068
O	0.347059	-0.079254	1.244033
V	-1.189438	0.060543	-0.000024
O	0.347090	-0.079645	-1.244000
O	2.674569	0.698808	-0.000077
O	-2.148886	-1.210421	0.000164
O	-2.010636	1.420068	-0.000248

tri-bridge

V	-1.171548	0.000365	-0.077977
O	-0.192496	1.248988	0.649740
V	1.156572	-0.000190	0.067163
O	-0.188719	-1.260183	0.626778
O	-2.748408	-0.001561	0.031926
O	2.734880	-0.002261	0.176032
O	0.437799	0.014515	-1.453388

NbO_2

NB	0.000000	0.000000	0.292138
O	0.000000	1.371082	-0.748604
O	0.000000	-1.371082	-0.748604

NbO_2^+

NB	0.000000	0.000000	0.291689
O	0.000000	1.325982	-0.747453
O	0.000000	-1.325982	-0.747453

NbO_3

NB	-0.213289	0.029205	0.000000
O	0.364368	-1.823089	0.000000
O	0.364368	0.836707	1.426924
O	0.364368	0.836707	-1.426924

NbO_3^-

NB	0.000000	0.000000	0.096713
O	0.000000	1.781642	-0.165219
O	-1.542947	-0.890821	-0.165219
O	1.542947	-0.890821	-0.165219

$NbO_2(OH)$

O	1.005410	-1.346219	0.366723
O	0.803803	1.472177	0.335068
O	-1.829734	-0.170817	0.214507
H	-2.446055	0.462982	0.596754
NB	0.063664	-0.002539	-0.193345

NbF_5

NB	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.884234
F	0.000000	1.853896	0.000000
F	1.605521	-0.926948	0.000000
F	0.000000	0.000000	-1.884234
F	-1.605521	-0.926948	0.000000

Nb_2O_5 isomers

mono-bridge

NB	0.000000	1.929996	0.108800
O	0.000000	0.000000	0.356595
NB	0.000000	-1.929996	0.108800
O	0.127085	2.435681	-1.541485
O	-1.402043	2.673398	0.805585
O	-0.127085	-2.435681	-1.541485
O	1.402043	-2.673398	0.805585

di-bridge

O	0.058373	-0.341701	1.298496
O	-1.319667	-2.564561	0.000000
O	0.058373	-0.341701	-1.298496
O	1.541977	2.261350	0.000000
NB	0.058373	1.356132	0.000000
NB	0.130712	-1.636582	0.000000
O	-1.308115	2.423922	0.000000

tri-bridge

O	0.000000	1.519574	0.000000
O	1.315989	-0.759787	0.000000
O	-1.315989	-0.759787	0.000000
O	0.000000	0.000000	3.002013
NB	0.000000	0.000000	-1.272725
O	0.000000	0.000000	-3.002013
NB	0.000000	0.000000	1.272725

TaO_2

TA	0.000000	0.000000	0.186530
O	0.000000	1.380633	-0.851045
O	0.000000	-1.380633	-0.851045

TaO_2^+

TA	0.000000	0.000000	0.187856
O	0.000000	1.336562	-0.857092
O	0.000000	-1.336562	-0.857092

TaO_3

TA	-0.169721	0.020732	0.000000
O	0.516236	0.776064	1.428011
O	0.516236	0.776064	-1.428011
O	0.516236	-1.741304	0.000000

TaO_3^-

TA	0.000000	0.000000	0.116555
O	0.000000	1.740051	-0.354521
O	-1.506928	-0.870026	-0.354521
O	1.506928	-0.870026	-0.354521

TaO_2(OH)

O	0.982186	-1.304569	0.535049
O	0.659609	1.499435	0.484783
O	-1.806264	-0.225371	0.301444
H	-2.393769	0.380736	0.764651
TA	0.050815	-0.001873	-0.155272

TaF_5

TA	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.886116
F	0.000000	1.856926	0.000000
F	1.608145	-0.928463	0.000000
F	0.000000	0.000000	-1.886116
F	-1.608145	-0.928463	0.000000

Ta_2O_5 isomers

mono-bridge

TA	0.000000	1.907522	0.058165
O	0.000000	0.000000	0.345244
TA	0.000000	-1.907522	0.058165
O	-0.229711	2.268788	-1.627801
O	-1.353161	2.580260	0.924425
O	0.229711	-2.268788	-1.627801
O	1.353161	-2.580260	0.924425

di-bridge

TA	-0.103930	-1.583800	0.000000
O	-0.023076	-0.281668	1.291600
TA	-0.023076	1.394962	0.000000
O	-0.023076	-0.281668	-1.291600
O	1.384267	-2.460193	0.000000
O	-1.534675	2.278522	0.000000
O	1.355491	2.468156	0.000000

tri-bridge

O	0.000000	1.516238	0.000000
O	1.313101	-0.758119	0.000000
O	-1.313101	-0.758119	0.000000
O	0.000000	0.000000	3.014305
TA	0.000000	0.000000	-1.273826
O	0.000000	0.000000	-3.014305
TA	0.000000	0.000000	1.273826

PaO_2

PA	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.815664
O	0.000000	0.000000	-1.815664

PaO_2^+

PA	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.777936
O	0.000000	0.000000	-1.777936

PaO_3^-

PA	0.000000	0.000000	0.104670
O	0.000000	1.875528	-0.396875
O	-1.624255	-0.937764	-0.396875
O	1.624255	-0.937764	-0.396875

PaO_3^-

PA	0.000000	0.000000	0.000000
O	0.000000	1.951848	0.000000
O	1.690350	-0.975924	0.000000
O	-1.690350	-0.975924	0.000000

PaO_3

PA	0.000000	0.000000	0.090601
O	0.000000	0.000000	-1.903827
O	0.000000	1.817880	0.436620
O	0.000000	-1.817880	0.436620

$PaO_2(OH)$

PA	0.000000	0.131283	0.000000
O	-0.117575	-2.024595	0.000000
O	-1.790708	0.552670	0.000000
O	1.834631	0.313545	0.000000
H	0.589220	-2.679688	0.000000

PaF_5

PA	0.000000	0.000000	0.000000
F	0.000000	2.064655	0.000000
F	0.000000	0.000000	2.049128
F	-1.788044	-1.032327	0.000000
F	1.788044	-1.032327	0.000000
F	0.000000	0.000000	-2.049128

Pa_2O_5 Isomers

mono-bridge

PA	0.000000	0.000000	2.143664
O	0.000000	0.000000	0.000000
PA	0.000000	0.000000	-2.143664
O	0.000000	1.820697	2.450524
O	0.000000	-1.820697	2.450524
O	-1.820697	0.000000	-2.450524
O	1.820697	0.000000	-2.450524

di-bridge

O	0.068450	-0.075426	1.292441
PA	0.068450	-1.757723	0.000000
PA	0.039022	1.646787	0.000000
O	0.068450	-0.075426	-1.292441
O	-1.456184	-2.811930	0.000000
O	1.869014	2.079633	0.000000
O	-1.772226	2.145048	0.000000

tri-bridge

PA	0.000000	1.561347	-0.031674
PA	0.000000	-1.561347	-0.031674
O	-0.976054	3.046734	0.439301
O	1.269981	0.161754	-0.796348
O	0.000000	0.000000	1.434676
O	-1.269981	-0.161754	-0.796348
O	0.976054	-3.046734	0.439301